

CIRCULATION COPY
SUBJECT TO RECALL
IN TWO WEEKS

An Evaluation of Triple Quadrupole MS/MS for
On-Line Gas Analyses of Trace Sulfur Compounds
from Oil Shale Processing

Carla M. Wong
Richard W. Crawford
and
Richard A. Yost
University of Florida

This paper was prepared for submittal to
American Society for
Testing of Materials

Symposium Proceedings on
Characterization of Shale Oils

January 1985

Lawrence
Livermore
National
Laboratory

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

**An Evaluation of Triple Quadrupole MS/MS for On-Line Gas Analysis of
Trace Sulfur Compounds from Oil Shale Processing**

Carla M. Wong* and Richard W. Crawford

Lawrence Livermore National Laboratory

Livermore, California 94550

and

Richard A. Yost

University of Florida

Gainesville, Florida 32611

ABSTRACT: In order to effectively reduce sulfur gas content from shale processing to environmentally acceptable levels, H_2S , COS , SO_2 and CH_3SH plus trace sulfur compounds must be removed. Of these, the trace sulfur compounds have not been well characterized but should be known to ppm levels in order to optimize gas clean-up procedures. Most techniques for analysis of trace sulfur components in oil shale gases have limitations. The applications we describe using triple quadrupole mass spectrometric techniques (TQMS) appears to have overcome many problems of trace sulfur analysis.

Basically a TQMS produces a mass spectrum of a mass spectrum and is, therefore, highly sensitive, selective and specific. Tests on a Finnigan TQMS at the University of Florida and on a totally computerized TQMS designed at LLNL using pure standards, mixed gas standards and Fisher assay gas grab samples show that we can quantitatively as well as qualitatively detect the following components:

- | | |
|--------------------------------|--------------------------------------|
| 1. methyl mercaptan = <1 ppm | 6. carbon disulfide = 4 ppm |
| 2. ethyl mercaptan = 3 ppm | 7. dimethyl sulfide = 10 ppm |
| 3. n-propyl mercaptan = <1 ppm | 8. dimethyl disulfide = <1 ppm |
| 4. isopropyl mercaptan = 4 ppm | 9. thiophene = <1 ppm |
| 5. carbonyl sulfide = 1 ppm | 10. 2 or 3 methyl thiophene = <1 ppm |

For a rapidly changing gas stream, timing studies on the LLNL TQMS show that analytical results for 10 sulfur compounds (1000 readings on each parent and key daughter ions) can be acquired and quantitatively calculated in ~ 30 seconds. For kinetics studies, data on selected daughters for 10 compounds can be acquired in a total of 540 milliseconds.

KEY WORDS: mass spectrometry, thiophenes, thiols, air pollution, pyrite, oil shale, shale oil, corrosion reactions, reaction kinetics.

Introduction

The reactions of sulfur in oil shale processing are important for health and environmental considerations as well as for processing conditions. Gaseous sulfur compounds such as H_2S , CS_2 , and SO_2 are toxic atmospheric pollutants (1). Hydrogen sulfide (H_2S) is classified toxicologically as a secondary irritant to the mucous membranes. A far more significant systemic effect occurs from the absorption of the compound. H_2S acts directly on the nervous system, resulting in paralysis of the respiratory center and the olfactory system. The irritant action, as well as its influence on ferric hemoglobin, combine to contribute to death by asphyxiation.

Sulfur dioxide (SO_2) is an irritant which effects the mechanics of respiration. It increases flow resistance, decreases compliance and breathing frequency and causes bronchoconstriction.

Carbon disulfide (CS_2) is a neurotoxicant involving the central nervous system causing intellectual and behavior abnormalities. It produces polyneuritis and marked decrease in visual acuity.

NIOSH permissible exposure limits for an 8-hour work day for these compounds have been set at: 10 ppm for H_2S with 300 ppm being Immediately Dangerous to Life or Health (IDLH); 0.5 ppm for SO_2 , with 100 ppm IDLH; and, 1 ppm for CS_2 , with 500 ppm IDLH (2).

However, since the states have the right to enact more stringent standards than those set by the Federal government, Colorado has determined that SO_2 must not exceed 0.3 lb./barrel of oil produced and H_2S must not exceed $142 \mu\text{g}/\text{m}^3$ or 0.1 ppm per 1-hour average (3,4).

In addition to the atmospheric problems associated with sulfur gases, there are equipment degradation processes directly related to the chemical effects of H_2S and other reduced sulfur compounds such as mercaptans, thiophenes, COS and sulfides. These gases poison catalysts and cause corrosion, erosion and embrittlement of equipment leading to costly repairs and replacement. The corrosive effects appear to be highly temperature dependent having the least effect below 150°C , a moderate effect at retorting temperatures of $500\text{--}540^\circ\text{C}$ and a severe effect in the combustion area where temperatures are in excess of 1000°C (5-8).

Other problems associated with understanding sulfur gases in oil shale processing are the variability of the oil shale composition and the effect of different processing conditions on ultimate product formation and composition. These processes have been studied for H_2 , CO, CO_2 , CH_4 and various hydrocarbons (9). However, attempts to study the effects of these same parameters of variability of oil shale composition and processing conditions for sulfur containing compounds have been

inhibited in the past by lack of speed, selectivity or sensitivity of analytical methods. In general, the studies need to answer the questions of type and concentration of trace sulfur compounds in the pyrolysis gases and whether the origin of the sulfur is organic, i.e., from the oil of the shale, or inorganic i.e., from pyrite inclusions. Additionally, we need to characterize the chemical reactions leading to various trace sulfur species and develop kinetic models from their generation rates. These experiments have to be done in real time, on-line in a very complex mixture. For example, in the Mahogany Zone Green River formation shale, sulfur is found in pyritic form (75 percent), as sulfates (3 percent) and as organics (24 percent), with a total sulfur content of 0.7 weight percent (10,11). During retorting, sulfur is released primarily as H_2S with concentrations typically 1 to 15 percent, COS and methyl mercaptan with concentrations as high as 0.1 percent, and unknown amounts and types of trace sulfur compounds. Table 1 shows both the sulfur gas forms resulting from pyrolysis processes and the ease of their removal. Previous work has shown that gaseous sulfur compounds cannot be reliably analyzed via grab samples (12). Wall effects (adsorption, desorption) can be significant for these polar compounds. So, on-line monitoring where a continual gas flow conditions and equilibrates the walls of the sampling system to minimize sample loss, is the most reliable sampling technique. Additionally, by doing on-line monitoring, important marker compounds can be used as internal standards and monitored in real-time to indicate retort parameters and allow feedback control.

Typically, analysis of trace sulfur compounds in complex mixes has been accomplished on static liquid or solid samples in the past (13,14). In this paper we will evaluate triple quadrupole mass spectrometry, TQMS, (15) as a method for doing on-line trace sulfur analysis in a complex

pyrolysis gas mix. This technique offers new data in the study of the three main problems associated with oil shale processing: 1) The sulfur levels must be reduced in present processing schemes by a factor of 100 to meet Colorado emission standards (10); 2) Different gas treatment processes remove different sulfur gases to varying extents so it is necessary to completely characterize sulfur compounds to properly design a gas clean-up system (16); and, 3) Previous attempts to characterize these compounds have had limitations. Therefore, since the effective removal or utilization of these trace sulfur containing compounds relies upon their identification and quantification, the chemistry of the processes or reactions involved in their formation must be understood (17). This instrument has the speed of analysis time (milliseconds to seconds), the selectivity (ability to differentiate sulfur containing compounds from hydrocarbons in a complex pyrolysis gas mix) and the sensitivity (low ppm range) to study the problems of trace sulfur species in oil shale pyrolysis gases.

Procedure

Equipment - The instruments employed in this study were an LLNL designed totally computer controlled triple quadrupole mass spectrometer described elsewhere (18-20), and a triple quadrupole mass spectrometer/data system manufactured by Finnigan Corporation, Sunnyvale, CA. The mass spectrometers were operated under electron impact (70eV) conditions in the positive ion mode with argon of 99.9 percent purity as the collision gas in quadrupole region two for the daughter ion scans. The source pressure was 3×10^{-4} Pa (2×10^{-6} torr) and the CAD argon gas pressure was 0.1 Pa (0.8 millitorr). Samples were Fisher assay gas samples introduced via the direct inlet probe vacuum port.

Daughter Ion Scans - Collisionally activated dissociation (CAD) mass spectra of the parent ion with the molecular weight of the trace sulfur compound were obtained by setting quadrupole 1 to transmit the parent ion of interest. It was then passed through the collision cell (quadrupole 2) filled with argon, operating in RF only mode (transmitting all ions), and then by scanning quadrupole 3, all daughter ions produced in the collisionally activated dissociation process were analyzed.

Normal Mass Scans - Quadrupoles 1 and 2 were operated in RF only mode, passing all ions, which were scanned (analyzed) in quadrupole 3 to give a normal mass spectrum. This data was used to do peak ratioing for quantization of the trace sulfur gas species.

Samples and Standards - All Fisher assay gas samples were produced at LLNL on location where grab samples were then collected and taken to the University of Florida for comparative sensitivity and analytical specificity tests.

All pure standards were 99.9 percent from Aldrich, Milwaukee, Wisconsin and all mixed gas standards were analyzed grade purchased from Matheson Corp., Joliet, Illinois.

Experimental Work (Results)

Various analytical approaches have been tried in the past at LLNL for sulfur gas analysis. These include GC, GC/MS, IR, FTIR, laser-Raman, microwave rotational spectroscopy (MRS), pulsed fluorescence analyzers, gas indicator tubes (Gastec and Drager), and various mass spectrometers (quadrupole, magnetic sector, time-of-flight and triple quadrupole MS/MS). Of all these methods, only mass spectrometers had the speed, and reliability to do routine on-line analysis. However, for trace quantities of unknowns in a complex mix, spectral overlap and background

interferences cause a lack of sensitivity, selectivity and specificity in normal mass spectrometric techniques. Table 2 shows that only the TQMS exhibited the necessary specificity to do on-line quantitation of trace sulfur species at the low ppm level in complex pyrolysis gas mixes. Additionally, the TQMS does not require extensive sample pre-separations because it is basically a mass spectrometer which can analyze ions that have been previously mass selected by a normal quadrupole mass spectrometer. In essence, it produces a mass spectrum of a mass spectrum. It is extremely sensitive because background or "chemical noise" is reduced and it is extremely selective because the detected material must have both the correct parent mass and the correct fragmentation pattern. There are five operational modes as shown in Figure 1. In this paper we will be discussing modes 1, a normal mass spectrum, and 2, the daughter ions produced from collisionally activated fragmentation (CAD) of specific parent ions.

The additional criteria for an on-line monitor (besides sensitivity, selectivity and specificity) are: 1) That the sampling inlet must not degrade or fractionate the gases; 2) It must be simple, i.e., no sample handling or pre-separations required; and 3) It must have speed. Speed includes both data acquisition and data manipulation and interpretation to give analytical results that are available on-line.

The gas inlet system developed at LLNL (Figure 2), which meets the sampling requirements and can be interfaced to any mass spectrometer, has been described previously (21-23). Basically, this system reduces the fractionation of gases by use of a capillary followed by a low pressure splitter and a pinhole leak. Since rapid equilibration of the system and low chemical activity are important, all lines exposed to gases are made of glass or stainless steel and are heated; the sampling system is

attached to a large volume, moderately high pressure part of the process gas flow system; and, the flow of gas is maintained at 5-10 cc per minute through the capillary. Additionally, the gas is pre-treated before entering the capillary system to remove particulates and liquids but still not alter the gas composition. The system is very tight to preclude any air leaks since mercaptans are readily oxidized to disulfides in the presence of oxygen.

To insure accurate analysis of trace sulfur compounds in the presence of all other oil shale pyrolysate gases, we purchased mixed gas standards with trace sulfur species from 6 ppm to 233 ppm. Compounds with interfering ions (benzene and cyclohexane) were added at levels of 200 ppm and 2000 ppm respectively to determine the selectivity, specificity and sensitivity of the TQMS.

The operational conditions that were used to obtain the detection limits of the TQMS using these standards and samples are described below.

Figure 3 shows a normal mass spectra from the TQMS (operating mode 1) acquired by analyzing one of the mixed gas standards containing ~20 ppm of various trace sulfur compounds (thiophene, methyl mercaptan, ethyl mercaptan, dimethyl disulfide, COS, and carbon disulfide). It also contained ~2000 ppm of cyclohexane with the balance being nitrogen. To determine the thiophene (molecular weight 84) from the cyclohexane (molecular weight 84) in the presence of all the other compounds would be impossible in normal mass spectrometry because there is a peak at every mass. By operating the TQMS in daughter mode (mode 2), quadrupole 1 is set on mass 84, argon is let into the CAD region of quadrupole 2, and the daughter fragments from the collisionally activated decomposition of mass 84 of pure thiophene and pure cyclohexane are produced. As shown in Figure 4, there is a distinct difference in the two resulting daughter

spectra. The thiophene parent at 84 amu produces an ion at mass 58 and at mass 45 which are not common to the ions produced by fragmentation of the cyclohexane mass 84 parent peak. By analyzing the mixed gas standard in the same fashion, we are able to determine that thiophene is present from observing the peaks at 58 and 45 amu. The digital data enables us to calculate the instrument detection limits from this known mixed gas standard (Table 3). The data also show the agreement in sensitivity in the interlaboratory instrument comparison of the LLNL TQMS and the University of Florida Finnigan TQMS (Figure 4). (Slight differences in spectra are due to the fact that no attempt was made to standardize the instruments to each other. We operated each instrument in our respective normal operating fashion to analyze the same pure standard compounds. Calculated ratios show excellent agreement between the instruments for the standards.)

A second experiment was performed to quantitate the percentage of loss due to "grab sample" techniques using known gas standards as samples. These results were compared to on-line analysis of the same known gas standards. The primary mixed gas standards were analyzed by TQMS and the "grab-samples" were taken (in containers) from these large standard bottles. These "grab samples" were then analyzed after 1 hour, 8 hours, 24 hours, 1 week and 2 months. The original primary mixed gas standard bottles were analyzed at each time interval also. The results of these tests are shown in Table 4. It can be seen that trace sulfur gases decrease in concentration with time. For some, such as propyl mercaptan, the decrease after only one hour is significant.

The third experiment involved determining the detection limits of the TQMS for analysis of trace sulfur-gas species in the complex organic gas mixture represented by real Fisher assay oil shale pyrolysis gas samples.

Two samples were chosen. One (MFS-32), was a 32 gallon per ton Western shale from Rio Blanco Tract C-a, sampled within a metre of the richest part of the Mahogany Zone (depth of 432 ft.). The other, (MFS-34), was a 12 gallon per ton Eastern shale from the Cleveland member of Ohio shale in Northeast Kentucky. Pure standards for thiophene, 2-methyl thiophene, 3-methyl thiophene, isopropyl mercaptan and n-propyl mercaptan were analyzed. The two Fisher assay gas samples were analyzed, then spiked with known amounts of the pure standards and re-analyzed. The instrument sensitivity, specific daughter ion selective sensitivity for pure standards and the specific daughter ion selective sensitivity in a complex mix with sample interferences were calculated. Peak ratios, extrapolations from pure standards, spiked samples and the use of n-butane as an internal standard were used in the calculations. From these analysis and calculations, the TQMS can quantitatively, as well as qualitatively, detect these components in a complex shale gas mix at the same levels as the mixed gas standards. The normal mass spectrum of the Kentucky shale Fisher assay gas (MFS-34) showing the spectral overlap and complexity is shown in Figure 5. Figure 6 shows the daughter spectra from mass 84 to determine thiophene in the same Kentucky sample. It is readily apparent that both cyclohexane and thiophene are present. The analytical results for the two samples are shown in Table 5. From the data we showed in Table 4 of the analytical experiments done on standard gas "grab samples", we believe that the Fischer Assay Gas sample analyses are low by a factor of 2 to 6. This is to be expected since the Fischer Assay samples were over 2 months old by the time analysis were completed at both LLNL and the University of Florida.

Since on-line analysis gives greater analytical accuracy, the speed of the data acquisition and interpretation then become very important

because we are dealing with a dynamic process in oil shale retorting procedures.

On the LLNL designed triple quadrupole mass spectrometer all functions of instrument operation are under total computer control and data is acquired by peak jumping. Therefore, the slowest part of the data acquisition time is waiting for the electrometer settling time between peaks. We use a direct memory access (DMA) on the analog to digital converter (10 microseconds/conversion) for data acquisition. This makes it possible to scan 10 parents and all of the daughters from 20-100 amu for each parent while taking 1000 readings for each amu in a total of 8.64 seconds. For kinetics studies, we can speed the process further by looking at only selected daughters of a given parent. In general, 1 to 3 selected daughters from a given parent can give a definitive specificity for a particular compound. However, if we are conservative and look at five daughters for each parent, we can still take 1000 readings on each daughter for each of 10 parents in a total of 540 milliseconds. Actual timing tests were done by pyrolyzing solid samples of high explosives and other compounds on-line (24).

The most time consuming and operator intensive step of the entire data acquisition process is extraction of data from the files. This requires 20 seconds for operator information input; 1 second for computer extraction; 5 seconds for terminal plotting; and, 12 seconds to copy the plot. Therefore each graph or plot requires 40 seconds.

We did not do any on-line timing tests on the University of Florida TQMS system. However, the observed speed of analysis of the University of Florida commercial system was certainly adequate for on-line analytical processes.

Conclusions

Analytical results on two research grade triple quadrupole mass spectrometer systems substantiate the key issues for on-line analysis of trace sulfur species in complex oil shale pyrolysis gases. Both the commercial Finnigan system and the LLNL designed system had: 1) sensitivity---key compounds can be quantitatively detected at <10 ppm; 2) selectivity---specific ions can be monitored; 3) specificity---sulfur containing compounds are easily differentiated from hydrocarbons in MS/MS mode; 4) simplicity---no pre-separation is required; and 5) speed---data acquisition and interpretation times are well within on-line requirements. The sampling issue has been resolved on other systems at LLNL. The inlet system design for on-line analysis is crucial for quantitative gas analysis, but even more importantly, as illustrated from the analysis done on the "grab samples" from our mixed gas standards, considerable loss of trace sulfur species occurs in a very short period of time. Therefore, for unknown, complex pyrolysis gas mixtures, quantitation of "grab-samples" is difficult, (if not impossible) and at best, is unreliable.

Finally, existing commercial TQMS instruments are very expensive because they are designed as research tools with multiple operating modes, a variety of ionization methods and usually include a gas chromatograph for GC/MS/MS. For the typical on-line analyses, the speed and separatory power of a TQMS preclude the need for a GC; and, normal electron ionization followed by daughter mode analysis is usually sufficient. Based on experience at LLNL in building a totally computerized research grade instrument, we feel that an on-line instrument could be constructed for ~\$100,000. This reduced cost is due to: 1) a simpler source; 2) smaller vacuum pumps; 3) simple detector; 4) flow type inlet system (instead of a GC); 5) simpler electronic controls and; 6) dedicated computer programs.

Acknowledgements

The authors would like to thank Art Lewis, LLNL Oil Shale Project Leader and Charles Bender, Chemistry and Materials Sciences Department Head for encouragement and support on this project. We would also like to thank Alan Burnham for many helpful discussions and oil shale samples. Thanks also to Mary Singleton of LLNL for the Fischer assay "grab samples," and Dean Fetterolf and Neil Brotherton of the University of Florida for help in the TQMS analysis of the pyrolysis gas samples at that institution.

Work performed under the auspices of the U.S. Department of Energy at Lawrence Livermore National Laboratory under contract W-7405-ENG-48.

Reference herein to any specific commercial products by manufacturer does not imply its endorsement by the United States Government or the University of California. The opinions of authors expressed herein do not necessarily reflect those of the United States Government and shall not be used for advertising or product endorsement purposes.

References:

1. Casarett, L. J. and Doull, J., Ed., Toxicology, The Basic Science of Poisons, Macmillan Publishing Co., Inc., New York, pp. 62, 160, 205 and 300, 1975.
2. Mackison, F. W., Stricoff, R. S. and Partridge, L. J., Eds., Guide to Chemical Hazards, DHEW (NIOSH) Publication No. 78-210.
3. Colorado Air Quality Control Commission, Colorado Air Quality Control Act and Amendments 1979 (Title 25, Article 7, Air Pollution Control, HB No. 1109), Reproduced by Colorado Department of Health, Denver, CO., 1979.
4. Code of Federal Regulation, 40 CFR 52.21, U.S. Govt. Print Off., Washington, D.C. 1981.
5. Levy, A. V., "Metal Corrosion in Oil Shale Retorts", in Proceedings, Corrosion-Erosion-Wear of Materials in Emerging Fossil Energy Systems, A. V. Levy, Ed., National Association of Corrosion Engineers, Houston, TX., pp. 421-475, 1982.
6. Ficalora, P. J. and DeVan, J. H., "Thermochemistry of Fluidized Bed Atmospheres", in ref. 6, pp. 476-492.
7. Nagarajan, V., Wright, I. G. and Smith, R. D., "Morphology of Corrosion of Advanced Heat Exchanger Materials in Simulated FBC Deposits", in ref. 6, pp. 493-510.
8. Minchener, A. J., Lloyd, D. M., Cooke, M. J., "Considerations of a Possible Mechanism for the Corrosion of High Temperature Components in Atmospheric Coal Fired Fluidized Bed Combustors", in ref. 6, pp. 511-547.
9. Campbell, J. H. and Burnham, A. K., "Reaction Kinetics for Modeling Oil Shale Retorting", In-Situ, vol. 4, pp. 1-37, 1980.

10. Burnham, A. K., Taylor, R. W., "Occurrence and Reactions of Oil Shale Sulfur", 15th Oil Shale Symposium, April 28-30, 1982, Golden, Colorado, Lawrence Livermore National Laboratory, Report UCRL-87052.
11. Sklarew, D. S., Fruchter, J. S., Schoengold, D. M., Tompkins, M. R., and Morris, C. L., "Measurement of Sulfur Species in Offgas from Rio Blanco's Retort O Tract C-a, Colorado", Preliminary Report, Battelle-Pacific Northwest Laboratories, Richland, Washington, 1981.
12. Shults, W. D., Ed., Preliminary Results: Chemical and Biological Examination of Coal-derived Materials. ORNL/NSF/EATC-18, Oak Ridge National Laboratory, Oakridge, Tenn., 1976.
13. Hunt, D. F., Schabanowitz, J., Anal. Chem., 54, pp. 574-8, 1982.
14. Morgan, R. P., Steele, G., Harris, J. A., Adv. Mass Spectrom., 8B, pp. 1725-1728, 1979.
15. Yost, R. A., Enke, C. G., Anal. Chem., 50, pp. 81A-92A, 1978.
16. Kohl, A. L. and Riesenfeld, F. C., Gas Purification, 4th ed., Gulf Publishing Co., Houston, TX., 1979.
17. Burnham, A. K., "Sulfur Reactions in Oil Shale Processing," in Proceedings, Corrosion-Erosion-Wear of Materials in Emerging Fossil Energy Systems, A. V. Levy, Ed., National Association of Corrosion Engineers, Houston, Texas, 1982, pp. 401-420.
18. Wong, C. M., Crawford, R. W., Barton, V. C., Bowman, J. E., and Brand, H. R., "The Design of a Totally Computer-Automated Eclectic Triple Quadrupole MS/MS", Presented at the 29th Annual Conference on Mass Spectrometry and Allied Topics, Minneapolis, MN., May 24-29, 1981.

19. Crawford, R. W., Brand, H. R., Wong, C. M., Gregg, H. R., Hoffman, P. A. and Enke, C. G., "A Data Base Management System for MS/MS and other Multi-Dimensional Instruments", Presented at the 30th Annual Conference on Mass Spectrometry and Allied Topics, Honolulu, Hawaii, June 6-11, 1982.
20. Wong, C. M., Crawford, R. W. Barton, V. C., Brand, H. R. Neufeld, K. W. and Bowman, J. E., "Development of a Totally Computer-Controlled Triple Quadrupole Mass Spectrometry System", Lawrence Livermore National Laboratory, Report UCRL-88140, Rev. 1, Submitted to Review of Scientific Instruments, September 1982.
21. Crawford, R. W., Bedford, R. G., Wong, C. M., Brand, H. R. and Kishiyama, K. I., "Use of an Automated Mass Spectrometer for an Underground Coal Gasification Field Test", In: Dynamic Mass Spectrometry, D. Price and J. F. J. Todd, Eds., Heyden, London, Vol. 6, Chapter 16, pp. 195-211, 1981.
22. Crawford, R. W., Stump, R. K. and Frazer, J. W., "A Computerized Fully Automatic Analytical Mass Spectrometer Part 1: Mechanical Design", Lawrence Livermore National Laboratory, Report UCRL-50931 Part 1, September 1970.
23. Crawford, R. W., Stump, R. K. and Frazer, J. W., "A Computerized Fully Automatic Analytical Mass Spectrometer Part 2: Electronic Design", Lawrence Livermore National Laboratory, Report UCRL-50931 Part 2, May 1971.
24. Wong, C. M. and Crawford, R. W., "Analysis of Solids Using a Fully Computerized Quadrupole MS/MS", Presented at 182nd ACS National Meeting, Paper No. 124, New York, New York, August 23-28, 1981.

Table 1. Production and Removal of Sulfur Species in Process Gas.

Gas type	Quantity	Ease of Removal
H₂S	~ 99%	easy
COS	~ 1%	difficult
Mercaptans	~ 0.1%	unknown
Thiophenes	?	unknown
Disulfides	?	difficult
SO₂	50-500 ppm	easy

Table 2. Summary Trace Sulfur Detection Limits on Four Mass Spectrometers for Mixed Gas Standards-(ppm)

	(ppm) Sensitivity	H ₂ S	COS	Methyl Mercaptan	Thiophene	Methyl Thiophene
Magnetic	Pyrolysis Gas	*100	100	100	100	100
Sector	Mixed Gas Std.	*20	10	20	10	10
Time-of	Pyrolysis Gas	*250	100	200	100	50
Flight	Mixed Gas Std.	*25	15	40	20	10
Normal	Pyrolysis Gas	25	25	25	50	50
Quadrupole	Mixed Gas Std.	10	10	10	10	10
Triple	Pyrolysis Gas	2	1	<1	<1	<1
Quadrupole	and Mixed Gas Std.					

***Depends on number of times sample is run to passify inlet**

Table 3. Sulfur Gas Detection Limits on TQMS-(ppm).

methyl mercaptan	= <1 ppm	carbon disulfide	= 4 ppm
ethyl mercaptan	= 3 ppm	dimethyl sulfide	= 10 ppm
n-propyl mercaptan	= <1 ppm	dimethyl disulfide	= <1 ppm
isopropyl mercaptan	= 4 ppm	thiophene	= <1 ppm
carbonyl sulfide	= 1 ppm	2 or 3-methyl thiophene	= <1 ppm

Table 4. Effect of Bottle Type and Time on Grab Samples from Trace Sulfur Gas Mixes.

Mix SX - 12995

	<u>Main Tank</u>	<u>Aluminum Bottle</u>			
	<u>1hr-2mo</u>	<u>1 hr</u>	<u>8 hr</u>	<u>24 hrs</u>	<u>2 Mo</u>
methyl mercaptan	17	17	17	15	13
ethyl mercaptan	19	19	17	17	8
carbonyl sulfide	20	20	17	15	7
carbon disulfide	15	15	11	11	11
dimethyl disulfide	6	6	5	4	3
thiophene	6	6	4	4	3

Mix SX - 12995

	<u>Main Tank</u>	<u>Stainless Steel Bottle</u>			
	<u>1hr-2mo</u>	<u>1 hr</u>	<u>8 hr</u>	<u>24 hrs</u>	<u>2 Mo</u>
methyl mercaptan	17	17	15	13	3
ethyl mercaptan	19	19	17	16	10
carbonyl sulfide	20	20	17	16	9
carbon disulfide	15	14	10	10	10
dimethyl disulfide	6	5	5	5	4
thiophene	6	5	4	4	4

Mix SX - 13070

	<u>Main Tank</u>	<u>Aluminum Bottle</u>			
	<u>1hr-6d</u>	<u>1 hr</u>	<u>8 hr</u>	<u>24 hrs</u>	<u>6 days</u>
n-propyl mercaptan	18	13	11	13	3
dimethyl disulfide	22	19	16	18	9
2-methyl thiophene	15	10	8	7	2

Table 5. TQMS Analysis of Trace Sulfur Gas Species in Fischer Assay Gas Samples

-
- o Sample MFS-32 is a 32 gal/ton Western Shale from Rio Blanco Tract C-a shale, 432 feet deep.**

 - o Sample MFS-34 is a 12 gal/ton Eastern shale from Cleveland member of Ohio Shale from N. E. Kentucky.**

	Western shale MFS-32 (ppm)	Eastern shale MFS-34 (ppm)
Cyclohexane	1200	1900
Thiophene	3	63
N-propyl mercaptan	3	22
isopropyl mercaptan	3	25

Figure Captions

Figure 1. TQMS Operational Modes.

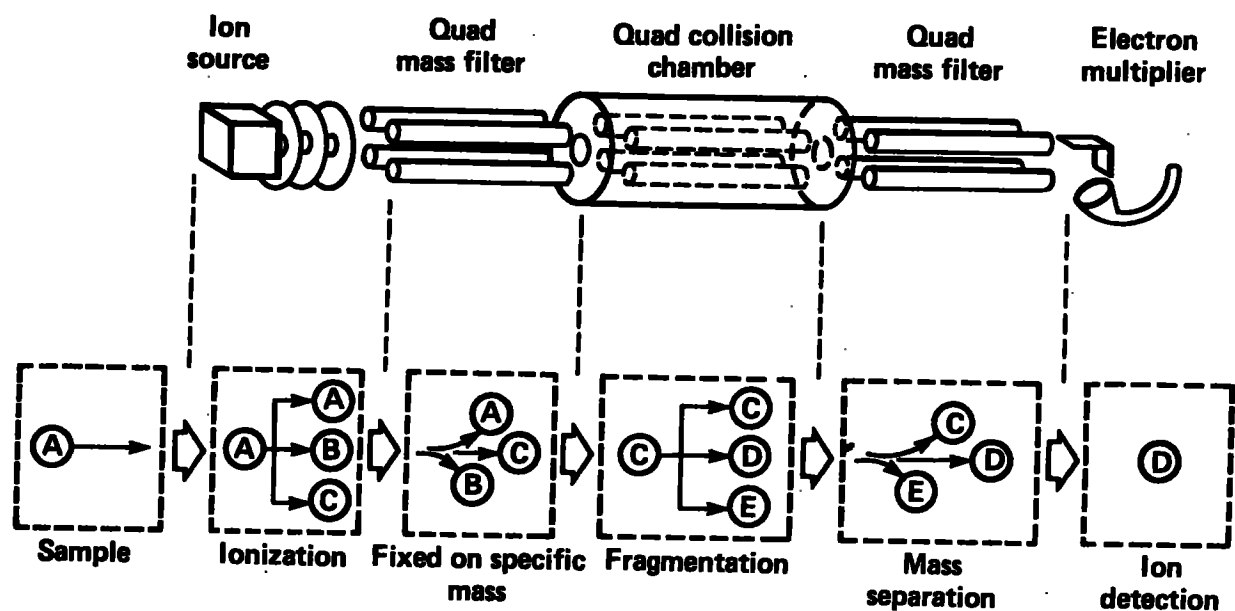
Figure 2. On-Line, Flow-Through Gas Inlet System.

**Figure 3. Normal Mass Spectra of 20 ppm Sulfur Gases + 2000ppm
Cyclohexane Standard Mix.**

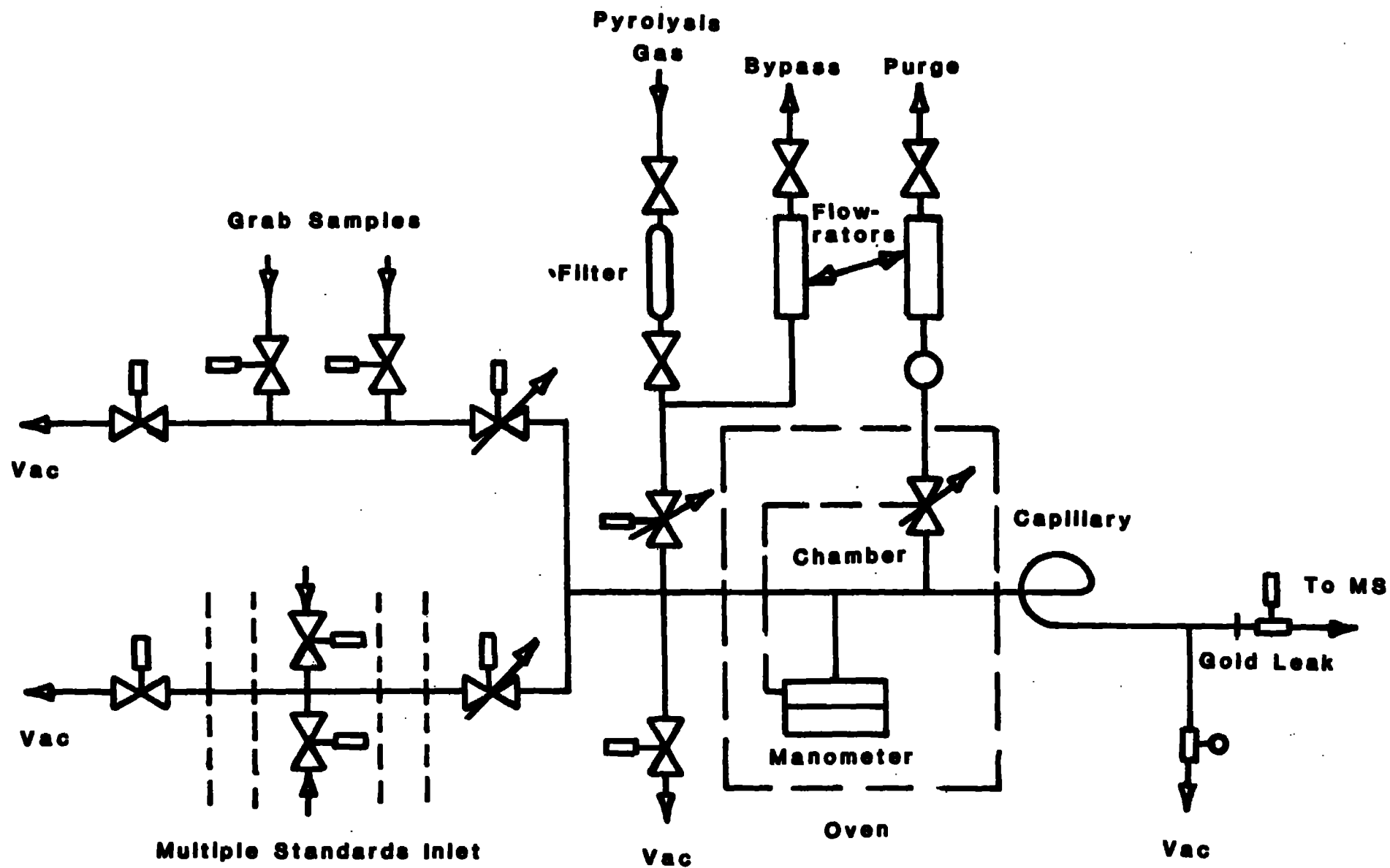
**Figure 4. Daughter Spectra of Interfering Ions at Mass 84 from LLNL and
University of Florida TQMS Systems.**

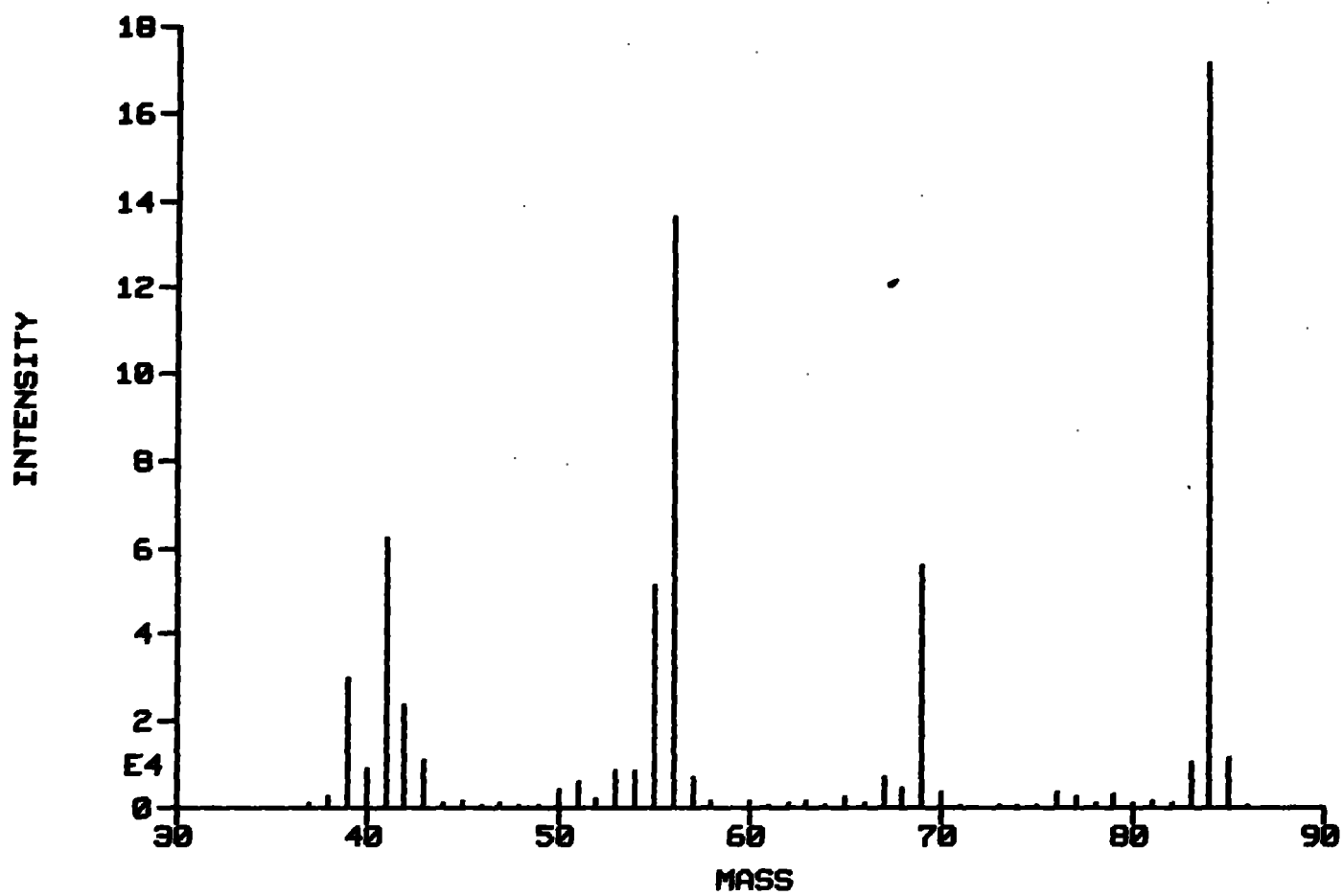
Figure 5. Normal Mass Spectra of Fischer Assay Gas Sample (MFS-34).

**Figure 6. Daughter Mass Spectra from Parent Ion 84 of Fischer Assay Gas
Sample (MFS-34).**

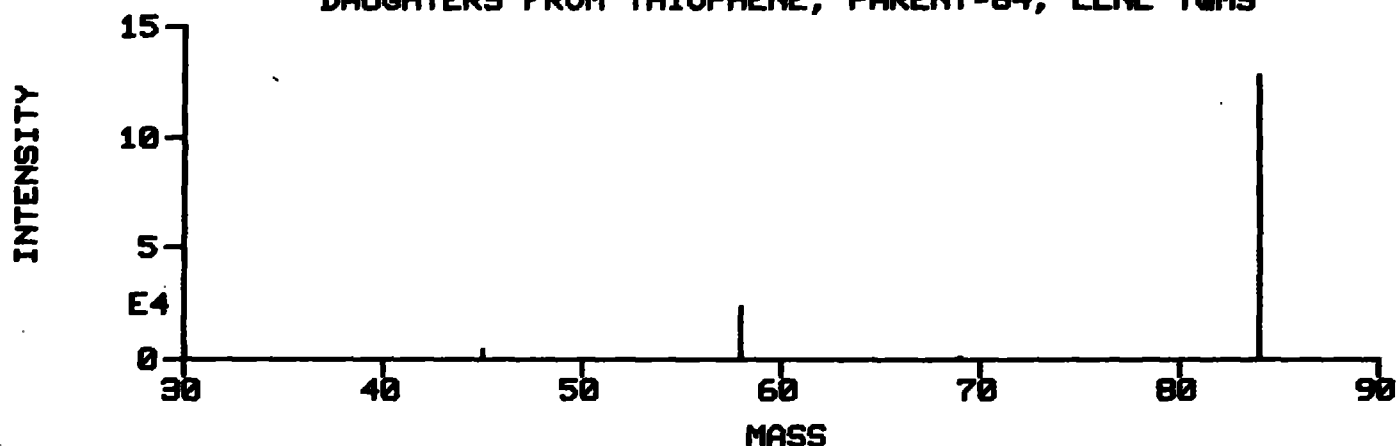


Operation Mode	Quad 1	Quad 2	Quad 3	Results
1	Separated by mass	All masses passed No gas	All masses passed	Normal mass spectrum
2	Fixed on specific mass	All masses passed Collision gas	Separated by mass	Spectrum of all daughter ions from the selected parent ion
3	Separated by mass	All masses passed Collision gas	Fixed on specific mass	Spectrum of parent ions that fragment to give specific daughter ion
4	Separated by mass	All masses passed Collision gas	Separated by mass	Fixed mass difference between 2 scanning quads gives specific neutral mass loss
5	Fixed on specific mass	All masses passed Collision gas	Fixed on specific mass	Single or multiple reaction monitoring

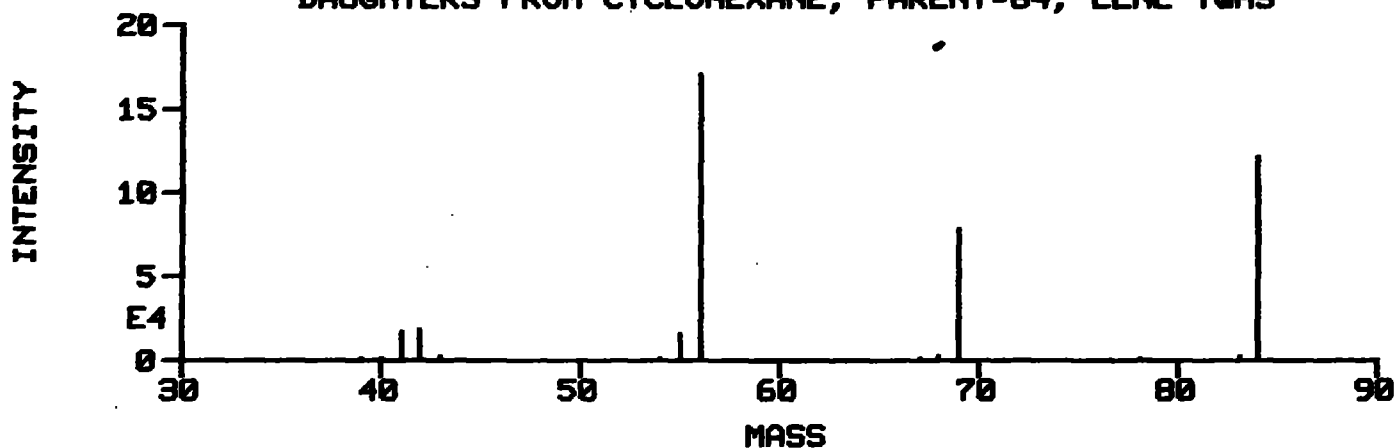




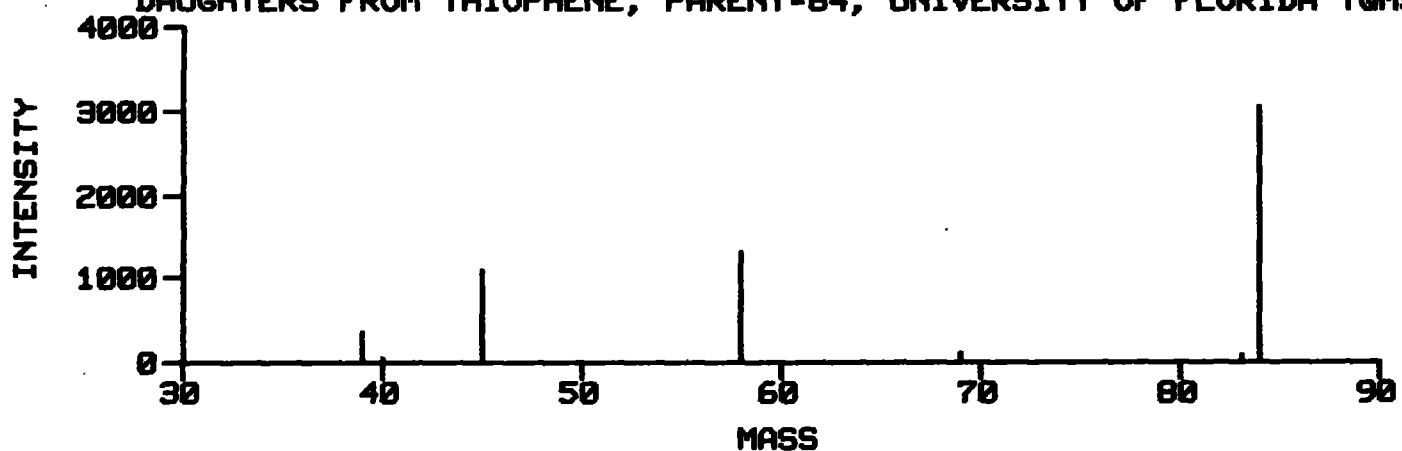
DAUGHTERS FROM THIOPHENE, PARENT-84, LLNL TQMS

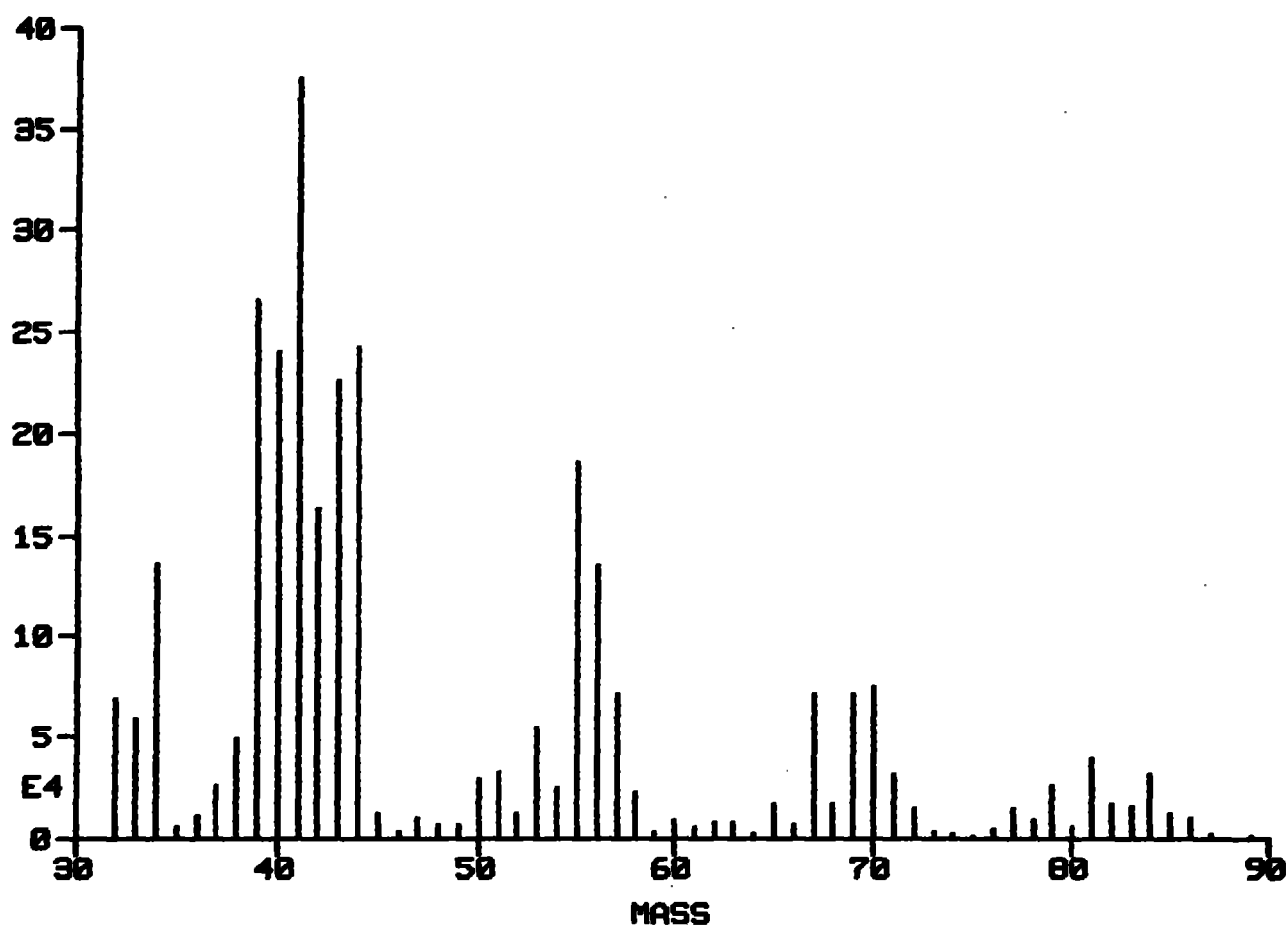


DAUGHTERS FROM CYCLOHEXANE, PARENT-84, LLNL TQMS

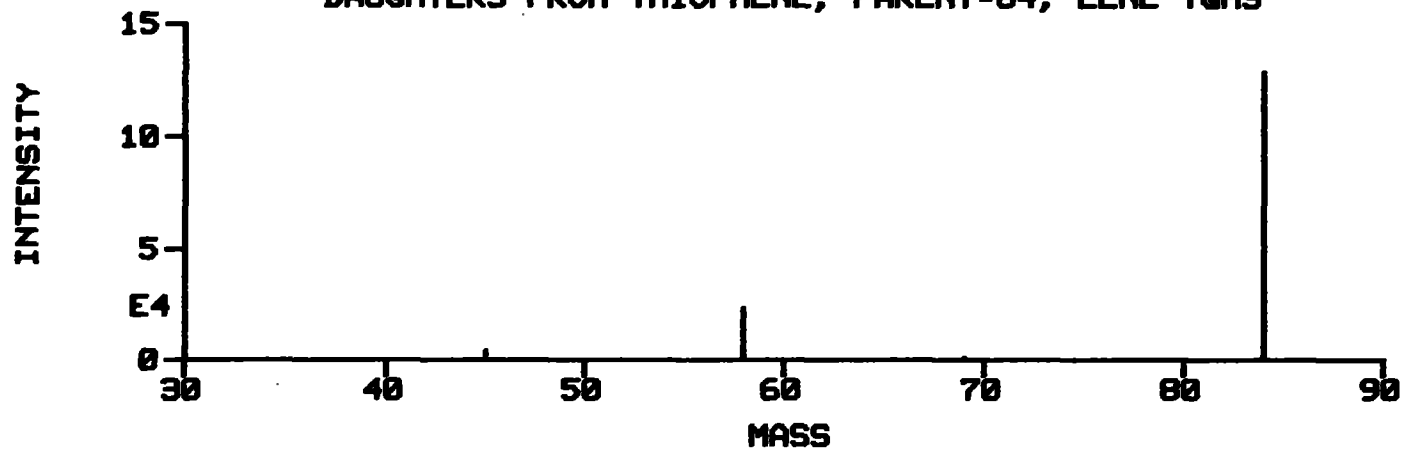


DAUGHTERS FROM THIOPHENE, PARENT-84, UNIVERSITY OF FLORIDA TQMS

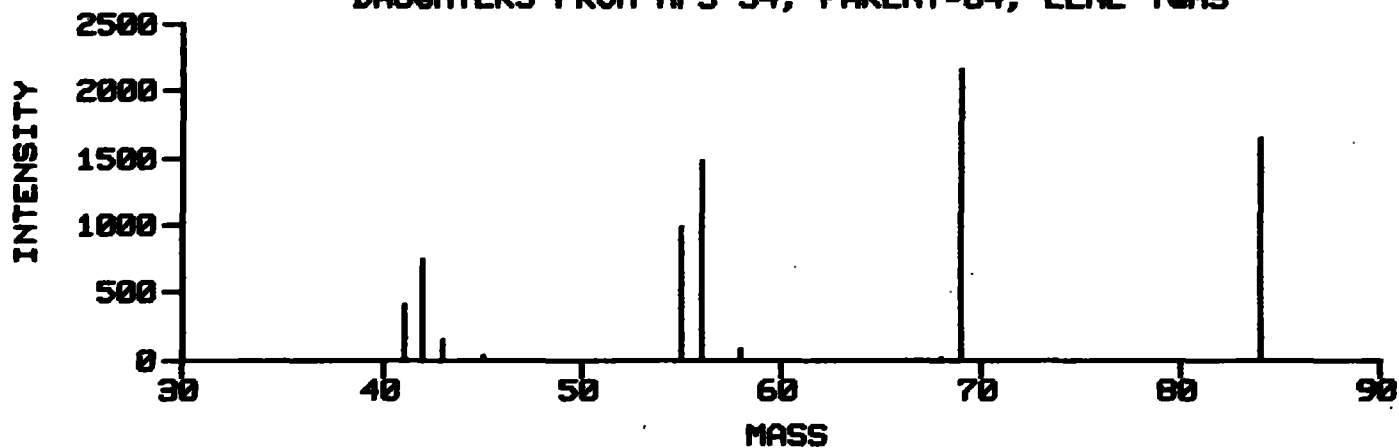




DAUGHTERS FROM THIOPHENE, PARENT-84, LLNL TQMS



DAUGHTERS FROM MFS 34, PARENT-84, LLNL TQMS



DAUGHTERS FROM MFS 34, PARENT-84, UNIVERSITY OF FLORIDA TQMS

